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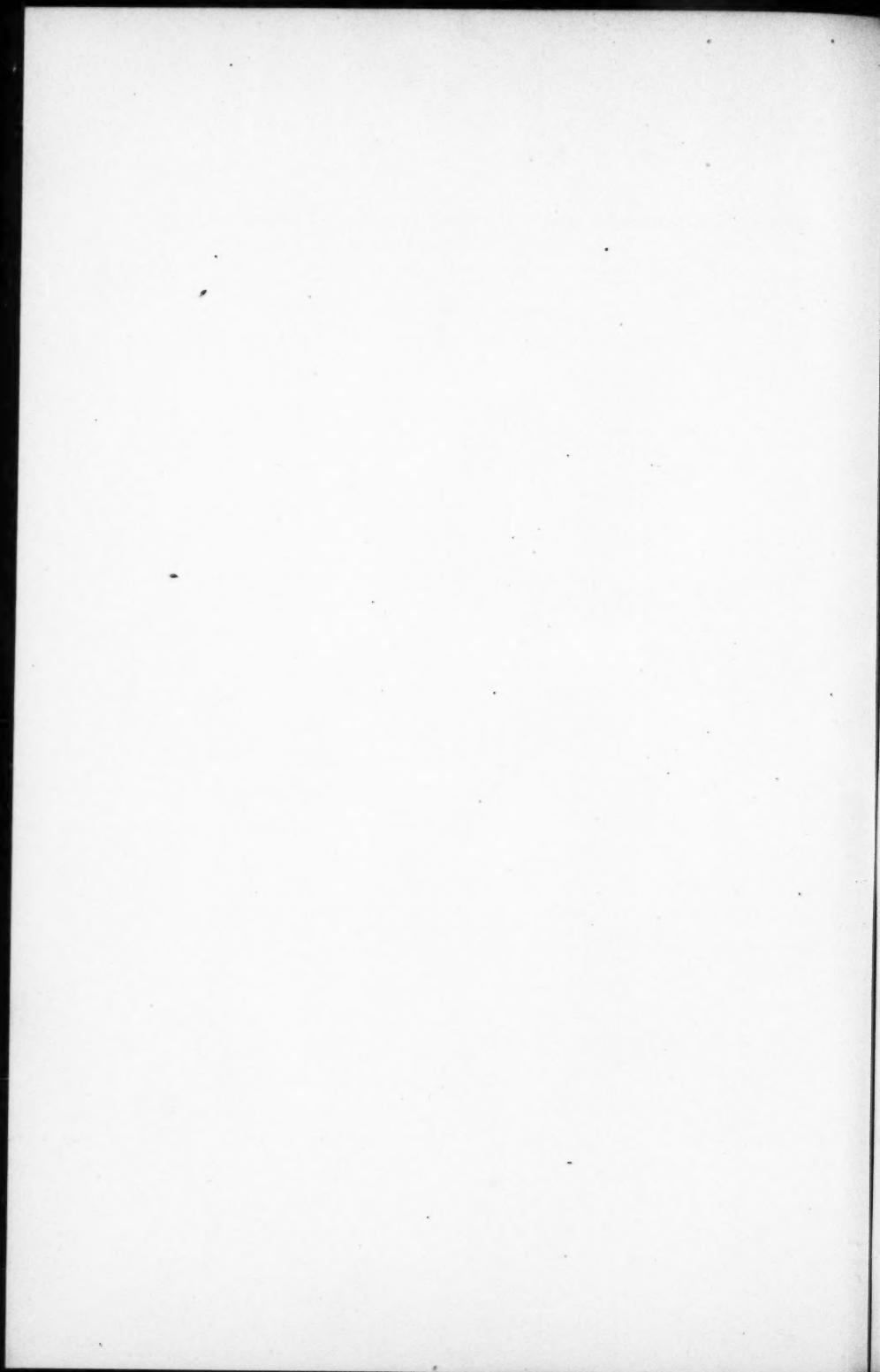
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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

*ON ELECTRIC CONDUCTION AND THERMOELECTRIC
ACTION IN METALS.*

EDWIN H. HALL.

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ON ELECTRIC CONDUCTION AND THERMOELECTRIC
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BY EDWIN H. HALL.

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Introduction.

VARIOUS considerations that I need not at the beginning set forth at length, but some of which will appear later in this paper, have led me to inquire whether we may not have, in the phenomena of electric conduction and of thermoelectric action in metals, the coöperation of electrons in two conditions. One condition, (*A*), I have conceived of as that of electrons passing from atom to atom of the metal so quickly, perhaps during actual contacts of the atoms, as not to become subject to the laws of gas pressure, the other condition, (*B*), I have thought of as that of electrons long enough free between the atoms to act according to the gas laws, though, in deference to the argument from radiation, I assume these free electrons to have a smaller kinetic energy of translation than gas molecules would have in a cavity within the metal.

Sir J. J. Thomson suggested in his *Corpuscular Theory of Matter*¹ an action somewhat like that which I imagine for the (*A*) electrons, though he seems presently to have abandoned this idea as unnecessary.² But since Thomson discussed the matter new experimental evidence, especially from the behavior of metals at low temperatures, has seemed to lead naturally back to the conception of electrons transmitted directly from atom to atom in metallic conduction. If we think of the atoms as being, at very low temperatures, in actual

¹ Pp. 49 and 50. "It is easy to see, however, that a current could be carried through the metal by corpuscles which went straight out of one atom and lodged at their first impact in another; such corpuscles would not be free in the sense in which the word was previously used and would have no opportunities of getting into temperature equilibrium with their surroundings." etc.

² See Tunzelmann's *Electrical Theory*, p. 301.

contact with each other much of the time, we have suggested at once an explanation of the vanishing electric resistance and the vanishing specific heat observed in pure metals as they approach the absolute zero of temperature. With atoms pressed very close together we should expect some of the electrons, what Rutherford would call the peripheral ones, to be movable from one atom to another with comparative ease, and with the same conditions we should expect the degrees of freedom of the atoms to be fewer,³ and the thermal capacity of the metal less, than at higher temperatures. A piece of metal in this condition, immersed in helium gas and subject to the impact of the gas molecules, may be compared to a brick building bombarded by tennis balls. If the individual bricks were free, they would absorb kinetic energy from the balls; but agglomerated in one huge mass they repel the attacks and remain almost unmoved.

On the other hand, thermo-electric phenomena appear to require the presence of free electrons within metals. In looking for a theory of electric conduction in solids we should not, even at the start, forget the fact that circuits exist in which the electric current is maintained at the expense of heat energy solely. Now, in all cases in which the transformation of heat into work is really understood, it is effected by means of change of dimensions, expansion and contraction of the working substance in which the heat resides and operates as molecular or atomic energy. In a thermo-electric current the electricity is the factor which undergoes a cyclic change; the metals are in a fixed state, though one of non-uniform temperature, and they neither expand nor contract after this fixed state is reached. It would seem, then, that the electricity must expand and contract in its cyclic course and serve as the vehicle and transformer of heat energy.

Hence my attempt to discover what a combination of the two kinds of electron action might be expected to do in a metal unequally heated. In the course of this undertaking, which has extended over some months, I have been led to change somewhat from time to time my point of view and the particular assumptions of which I have made use. For example, starting with the idea that the free electrons have a heat capacity which is constant, though much less than that of ordinary gas molecules, I later determined to try the experiment of taking this thermal capacity as a variable, increasing with rise of temperature but still, at ordinary temperatures, below that of gas

³ See Jeans, *Phil. Mag.*, Vol. 17 (1909)† p. 794, where the possibility that the atoms of a metal may have very little thermal capacity when locked together is discussed.

molecules.⁴ This innovation seems to be justified by its success in meeting certain requirements of the situation.

The conclusion to which my reflections, carried on with the help of some mathematical machinery, have led me is, that the free electrons, though present and essential for thermoelectric action, are of relatively small importance in mere electric conduction.

Fundamental Assumptions.

I shall assume that n , the number of free electrons per cu. cm. of the metal at any temperature, T absolute, can be expressed as $n = k_n T^\nu$, and that R , of the free-electron gas-equation $pv = RT$, "reckoned for a single electron,"⁵ can be expressed as $R = k_r T^\rho$, k_n , ν , k_r , and ρ being constants. These two assumptions give

$$Rn = k_r T^\rho \times k_n T^\nu = k T^q, \quad (1)$$

where k and q are constants.

For a single molecule of an ordinary gas the value of R is about 137×10^{-18} . I assume that R for an electron has a very much smaller value than this at low temperatures.

Whether any metal really satisfies the conditions indicated by (1) through any great range of temperature may well be doubted; but,

⁴ The "law of equipartition of energy," a law more familiar, perhaps, in the breach than in the observance, doubtless requires that electrons acting as gas particles among other gas particles of a different class shall attain the same mean translatory energy as the latter, provided the two classes of particles remain distinct from each other in their encounters. But if electrons collide with metal atoms containing or made up of electrons, and if during a collision it frequently or usually happens that the electron enters an atom and stays there, displacing another electron, there seems to be no reason for supposing that the mean translatory energy of the free electrons will equal that of the atoms.

⁵ Let us, for one gram of electrons, write $pv = R'T$. Then, taking m as the mass per electron and c as the "velocity of mean square," we have

$$p = \frac{1}{3} mnc^2 = R'T \div v = R'T mn.$$

From these relations we get

$$p = n(R'm)T = nRT,$$

an expression which will be used frequently hereafter, and

$$c \propto (RT)^{\frac{1}{2}}.$$

This proportionality must replace in this paper the simpler relation, $c \propto T^{\frac{1}{2}}$, which holds for an ordinary gas. This substitution is highly important. For example, if ρ of equation (1) is 1, so that $R \propto T$, we have $c \propto T$, and so $\frac{1}{2}mc^2 \propto T^2$; that is, the thermal capacity of the electron is $\propto T$, and its heat-energy content $\propto T^2$, if $\rho = 1$.

with freedom to make ρ and ν any constants whatever for any given metal, we should be able to represent the facts with considerable accuracy through moderate ranges of temperature, and we have under these conditions a field of possibilities which seems to be worth exploring.

Electric Conduction.

According to the ideas set forth in the preceding pages the specific conductivity of a metal is the sum of two parts, one due to the (A) electrons, the other to the (B), or "gas-kinetic," electrons. The first of these parts I shall represent as

$$K_a = F_1(\delta, T),$$

where F_1 is some function of δ , the mean distance between the centres of adjacent atoms of the metal, and of T , the absolute temperature of the metal.

I shall assume that previous discussions⁶ of free electron theory have been correct in taking that part of the conductivity which depends on the free electrons as proportional to n (in equation (1)) and to τ , the mean time between collisions of a free electron with the atoms. Evidently τ is equal to the free mean path, between such collisions, divided by the mean heat-velocity of the electrons. The mean free path is some function of δ ,— $F_2(\delta)$, let us say, which increases with rise of temperature under ordinary conditions, while the mean velocity⁷ is proportional to $(RT)^{\frac{1}{2}}$; so that $\tau \propto F_2(\delta) \div (RT)^{\frac{1}{2}}$; with $R = k_p T^\rho$, as in equation (1). Accordingly we get, as the part of the specific conductivity which depends on (B),

$$K_b = k_b T^\nu F_2(\delta) \div T^{\frac{1}{2}(\rho+1)} = k_b F_2(\delta) T^{(\nu-\frac{1}{2}\rho-\frac{1}{2})}. \quad (2)^b$$

For the total specific conductivity we now have

$$K = F_1(\delta, T) + k_b F_2(\delta) T^{(\nu-\frac{1}{2}\rho-\frac{1}{2})}. \quad (2)$$

When a metal is heated under ordinary conditions,—that is, at constant pressure with increase of volume, we have as the temperature coefficient of K

$$\begin{aligned} \alpha_p = \frac{dK}{KdT} &= \frac{1}{K} \left(\frac{\partial F_1}{\partial \delta} \right)_T \frac{d\delta}{dT} + \frac{1}{K} \left(\frac{\partial F_1}{\partial T} \right)_\delta \\ &+ \frac{k_b}{K} \cdot \frac{dF_2}{d\delta} \cdot \frac{d\delta}{dT} \cdot T^{(\nu-\frac{1}{2}\rho-\frac{1}{2})} \frac{k_b}{K} \cdot F_2(\delta) (\nu-\frac{1}{2}\rho-\frac{1}{2}) T^{(\nu-\frac{1}{2}\rho-\frac{1}{2})}. \end{aligned} \quad (3)$$

⁶ For example, see p. 303 of Tunzelmann's *Electrical Theory*.

⁷ See footnote, p. 69.

This quantity, as a whole, must have a negative value, if it is to accord with the experimentally known facts; but as to the signs of its separate terms there may be some question. It seems plain that the first term is negative and that the third term is positive. The second term, if there were no evidence to the contrary, I should take as positive, and at first I did so take it, believing that I had experimental ground, as well as a *priori* ground, for this belief. The experimental ground proved not to be good footing, and I am now inclined to the opinion that this term is negative, for reasons which will presently appear. The fourth term evidently has the sign of its factor $(\nu - \frac{1}{2} \rho - \frac{1}{2})$. Now according to my discussion of the Thomson effect (see equations (15)–(21)) this factor is probably positive in many metals, and, as the third term of α_p is obviously positive, we reach the conclusion that, in these metals at least, the negative value of the temperature coefficient α_p cannot be accounted for if the electric conduction within these metals is solely, or even mainly, by means of the (*B*) electrons. We are thus led to attach especial importance to the first term in the value of K , as given in equation (2), and to the first two terms in the values of α_p , as given in equation (3).

In seeking further light on the term $\frac{1}{K} \frac{\partial F_1}{\partial T}$, the sign of which has thus far been left in doubt, we naturally turn to such experiments as show the effect of increased pressure on the electric conductivity of metals. We have at command the data for calculating, in the case of several metals, approximately what the temperature coefficient of the conductivity would be if heating occurred with such increase of pressure as to keep the volume of the metal constant. If we call this coefficient α_v , and if we assume that we can find an expression for it by merely dropping from the value of α_p the two terms which contain the factor $d\delta \div dT$, we have

$$\alpha_v = \frac{1}{K} \frac{\partial F_1}{\partial T} + \frac{k_b}{K} \cdot F_2(\delta) (\nu - \frac{1}{2} \rho - \frac{1}{2}) T^{(\nu - \frac{1}{2} \rho - 2)}. \quad (3a)$$

In liquid mercury, according to the experiments of Barus,⁸ the value of α_v is positive; but in the solid pure metals, so far as I know, it is negative and, though numerically less⁹ than α_p , not very much less. If, then, equation (3a) is a correct expression for α_v , it appears that the term $\frac{1}{K} \frac{\partial F_1}{\partial T}$ is negative, since the second term, as we have seen, is probably positive.

⁸ Bulletin of the U. S. Geol. Survey, No. 92 (1892), p. 75.

⁹ See the Appendix to this paper for discussion of this matter.

The Thermodynamic Point of View.

The greater part of my argument from here on will lie in a thermodynamic treatment of thermoelectric action, and in the course of it I shall make free use of the fact, which I have pointed out in previous¹⁰ papers, that the ordinary thermoelectric diagram, representing "thermoelectric heights" as functions of temperature, is in reality a temperature-entropy diagram. Following ordinary engineering practice, I shall take the temperature coördinate as vertical and the entropy coördinate as extending horizontally toward the right.

Putting aside for the present the consideration of part (A) of the electric current, I shall discuss part (B) at some length as if it existed alone, returning to the treatment of (A) later.

Several years ago I discussed the analogy which exists between the cycle described by water in the circuit of a heating system, or in the circuit of a steam engine, and the cycle described by electricity in a thermoelectric circuit. The motion of the water in each of the cases referred to is, of course, due to heat, but heat alone would not maintain circulation. The application or expenditure of the heat must be managed or maneuvered by agents which do none of the net work of the cycle. In the case of the steam engine this control is given by a system of valves, or checks which permit movement in one direction but not in the other. In the heating system, valves and checks may be dispensed with, gravity exercising what in chemistry would be called the catalytic function of maintaining the desired action, circulation, at the expense of heat. In the thermoelectric circuit we must look for some agency to perform a like service. Thus, if we have a detached piece of copper with one end at temperature T and the other at a lower temperature T' , a state of equilibrium exists within it such that there is no electric flow along the metal; it is the same with a detached piece of iron wire having its ends at the same temperatures, T and T' ; but, if we join the warm end of the copper to the warm end of the iron and the cold end of the copper to the cold end of the iron, we find that a current of electricity flows from copper to iron at one junction and from iron to copper at the other junction. It is quite evident that, if we had to do with electric potential only, in the ordinary sense of the term, either there would be no flow on bringing the wires into circuit or there would be flow in the same direction at both

¹⁰ For example, These Proceedings, 46, 649 (1911).

junctions. Let us therefore consider carefully what may be the nature of the equilibrium which exists in a detached piece of wire having a temperature gradient.

The Boltzmann Aërostatic Equation.

I shall make use of the idea that each metal exercises a specific "intrinsic" attraction for electrons. Helmholtz long ago assumed such an attraction¹¹ for electricity in discussing the "double layer" at the surface between different substances. Several years since I made the suggestion that this attraction might be a function of the temperature of the metal. More recently O. W. Richardson¹² has made use of the Boltzmann formula

$$\frac{n_1}{n_2} = e^{-\frac{W}{RT}} \quad (4)$$

in dealing with the forces exerted upon electrons by electrical charges or by the attracting metal atoms. In this formula " n_1 is the concentration of the electrons at a point A and n_2 that at a point B ," and " W is the work done in taking an electron from A to B and R is the gas constant in the equation $p\theta = R\theta [= RT]$, reckoned for a single electron."

I feel greatly indebted to Professor Richardson for his discussion of this matter, and when I took up the question now before us I expected to use his ideas and conclusions, except in so far as they might be modified by my assumption that R for an electron is less than R for a gas molecule. I have, however, upon close examination of the matter, been forced to the conclusion that, in applying formula (4) to a discussion of the Thomson effect, involving of course a difference of temperature between the two points A and B , he has fallen into error.

Boltzmann gives the equivalent of the formula in question under the heading *Aërostatik*,¹³ and it is very easily derived, as follows, for an atmosphere of uniform temperature in equilibrium:

¹¹ This at least is my interpretation of certain passages in his papers; for example, the following sentence from an article in the *Monatsbericht d. k. Akad. d. Wiss. zu Berlin*, Nov. 3, 1881, S. 951: "Soll in einen Leiter, dessen Potential (elektrostatisch gemessen) p und dessen galvanische Constante k ist, ein neues Quantum Elektrizität dE eingeführt werden, so ist dazu die Arbeit $(p-k) dE$ nothig."

¹² Phil. Mag., Vol. 23 (1912), pp. 263-278.

¹³ Gastheorie, Vol. I, § 19.

Let l = height above the earth's surface,

ρ = density of the gas,

p = pressure " " "

g = gravity acceleration,

R' = gas constant for unit mass,

T = absolute temperature.

Then $-\frac{dp}{dl} = g\rho = g\frac{p}{R'T}$, whence

$$\frac{dp}{p} = -\frac{g}{R'T}dl, \text{ and so } \log p = -\frac{g}{R'T}l + \log k,$$

or $p = k\epsilon^{-\frac{gl}{R'T}}$, where k = pressure at the earth's surface.

Then for any two points A and B , with pressures p_1 and p_2 respectively, and molecular concentrations n_1 and n_2 respectively, we have

$$\frac{p_2}{p_1} = \frac{n_2}{n_1} = \epsilon^{-\frac{g(l_2 - l_1)}{R'T}} = \epsilon^{-\frac{W'}{R'T}}.$$

In this equation W' is the work of lifting unit mass from l_1 to l_2 against the pull of gravity. If we wish to deal with a single molecule of mass m , we can write

$$\frac{p_2}{p_1} = \frac{n_2}{n_1} = \epsilon^{-\frac{W'm}{R'mT}} = \epsilon^{-\frac{W}{RT}},$$

which is the Boltzman equation as used by Richardson.

Thermoelectric Equilibrium in a Detached Wire

(with consideration of (B) electrons only).

In dealing with the free electrons in a metal unequally heated we have a case somewhat like the one just discussed but considerably more complicated. In place of g we must now put f' , the resultant of attractions and repulsions per gram of free electrons, this resultant being called positive when it is directed along the path of diminishing l , and we must consider f' as a variable. In place of R' for a gram of gas we must put R' for a gram of free electrons, and take R' as a variable according to equation (1). Moreover T is now to be taken as a variable along l . We shall write

$$\beta = dT \div dl,$$

and shall treat β as a variable.

Now in place of the equation $\frac{dp}{p} = -\frac{g}{R'T} dl$ we have

$$\frac{dp}{p} = -\frac{f'}{R'T} dl = -\frac{f'}{R'\beta} \cdot \frac{dT}{T}.$$

But $p = R'Tnm$, and so

$$\frac{dp}{p} = \frac{dR'}{R'} + \frac{dn}{n} + \frac{dT}{T} = -\frac{f'}{R'\beta} \cdot \frac{dT}{T},$$

whence
$$\frac{dR'}{R'} + \frac{dn}{n} = -\left(\frac{f'}{R'\beta} + 1\right) \frac{dT}{T},$$

or, if we multiply both R' and f' by m , and so get R and f for a single electron,

$$\frac{dR}{R} + \frac{dn}{n} = -\left(\frac{f}{R\beta} + 1\right) \frac{dT}{T}. \quad (5)$$

When we observe that f , β , and R are all variables, the integration of this equation appears at first to present difficulties. But two of our fundamental assumptions, expressed in equation (1), give $Rn = kT^q$, where k and q are constants, and the only way to make this equation agree with equation (5) is to have the factor $\left(\frac{f}{R\beta} + 1\right)$ a constant. Thus we get by the integration of (5)

$$Rn = kT^{-\left(\frac{f}{R\beta} + 1\right)} = kT^q, \quad (6)$$

and so

$$\frac{n_2}{n_1} = \left(\frac{T_2}{T_1}\right)^q \dots \dots \dots (7)$$

In dealing with our detached piece of wire I shall use F to indicate *virtual* potential for a single electron,—that is, the total potential due to attractions and repulsions of electric charges *together with the attractions of the metal atoms*,¹⁴ as exerted on a single electron. If the distance l is measured from the cold end of the wire, we have

$$f = \frac{dF}{dl}, \text{ and } \beta = \frac{dT}{dl}, \text{ so that } \frac{f}{\beta} = \frac{dF}{dT}. \quad (8)$$

We have seen that equation (6) is a necessary consequence of equations (1) and (5). As (1) expresses merely certain fundamental

¹⁴ If the assumption of an attraction of the metal for the electrons, as a function of temperature, were omitted, the word *virtual* as applied to the potential would be omitted.

assumptions, our only question here is whether (5) is necessarily true. Examination shows that it involves the assumption, not explicitly made thus far, that the free electrons in unequally heated metal *tend* toward equality of gas-pressure, that the difference dp , between two isothermal planes differing by dT , must be balanced, if we are to have equilibrium, by the force f , applied to every free electron between the planes.

This assumption, which implies that the free electrons tend to the condition

$$n_1 R_1 T_1 = n_2 R_2 T_2, \quad (9)$$

where the subscripts (1) and (2) refer to any two parts of the metal, is by no means a matter of course when we are dealing with a gas permeating narrow passages where differences of temperature exist.

It is well known that, if a thin partition pierced only by a very small hole separates two bodies of an ordinary gas, one at temperature T_1 , the other at temperature T_2 , the condition of equilibrium between the two bodies of gas is not equality of pressure, but $p_1 \div p_2 = T_1^{\frac{1}{2}} \div T_2^{\frac{1}{2}}$, or, since $p_1 : p_2 :: n_1 T_1 : n_2 T_2$,

$$n_1 T_1^{\frac{1}{2}} = n_2 T_2^{\frac{1}{2}}.$$

That is, there is a certain tendency of the gas from the cold chamber to the warm chamber, which must in the end be balanced by superior pressure in the warm chamber.¹⁵

Going to the case of electrons, for which we assume R to be a variable, we have as the law of equilibrium under thermal effusion alone

$$n_1 (R_1 T_1)^{\frac{1}{2}} = n_2 (R_2 T_2)^{\frac{1}{2}}, \quad (9')^{16}$$

or, since $p = nRT$, $p \propto (RT)^{\frac{1}{2}}$.

¹⁵ Maxwell, toward the end of his memoir on *Stresses in Rarefied Gases*, says, "The passage of gases through porous plates, as was shown by Graham, is of an entirely different kind from the passage of gases through capillary tubes, and is more nearly analogous to the flow of a gas through a small hole in the thin plate."

"When the diameter of the hole and the thickness of the plate are both small compared with the length of the free path of a molecule, then, as Sir William Thomson has shown, any molecule which comes up to the hole on either side will be in very little danger of encountering another molecule before it has got fairly through to the other side."

"The finer the pores of a porous plate, and the rarer the gas which effuses through it, the more nearly does the passage of a gas through the plate correspond to what we have called effusion." etc.

¹⁶ For, another way of stating the condition of equilibrium in the case of thermal effusion is, that the *momentum* of the particles per cu. cm. shall be the same at one place as at another. If we take c as the "velocity of mean square," this condition gives $n_1 c_1 = n_2 c_2$, and we have already seen, in the footnote on p. 69, that $c \propto (RT)^{\frac{1}{2}}$.

The differential expression of this law is

$$dp = \frac{p}{2} \frac{dR}{R} + \frac{p}{2} \frac{dT}{T} \quad (10)$$

That is, the difference of pressure which the free electrons in a stratum of thickness dl can bear without drift, and without the help of electrical force, is

$$\frac{p}{2} \frac{dR}{R} + \frac{p}{2} \frac{dT}{T}.$$

If the difference of pressure on the two faces of the stratum is greater than this quantity, we must, in order to have equilibrium, balance the excess of dp by the electrical force $-fndl$ acting up the temperature incline. Thus we get

$$dp = \frac{p}{2} \frac{dR}{R} + \frac{p}{2} \frac{dT}{T} - fndl,$$

whence, as

$$n = p \div RT, \text{ and } \beta = dT \div dl,$$

we have

$$\frac{dp}{p} + \frac{f}{R\beta} \cdot \frac{dT}{T} = \frac{1}{2} \frac{dR}{R} + \frac{1}{2} \frac{dT}{T}.$$

As $p = nRT$, we get from this equation, by substituting for p and dp ,

$$\frac{1}{2} \frac{dR}{R} + \frac{dn}{n} = - \left(\frac{f}{R\beta} + \frac{1}{2} \right) \frac{dT}{T}. \quad (5')$$

Now the assumptions which give equation (1) give also the equation

$$R^{\frac{1}{2}} n = k_c^{\frac{1}{2}} T^{\frac{5}{2}} \times k_n T^{\nu} = k' T^{q'}, \quad (1')$$

and in order to make (5') and (1') agree we must, as in the case of equation (5), treat $(f \div R\beta)$ as a constant. Accordingly we have

$$R^{\frac{1}{2}} n = k_r' T^{-\left(\frac{f}{R\beta} + \frac{1}{2}\right)} = k' T^{q'}, \quad (6')$$

where k' and q' are constants.

Not knowing which of the two conditions, (9) or (9'), represents the gas-pressure tendency of the free electrons the more nearly, I shall try each of the two corresponding equations, (6) and (6'), in turn. But before doing this, I must call attention to the fact that neither form of this tendency can make any great change in what we may call the natural values of n_1 and n_2 ,—that is, the values which would be found in two detached pieces of the same metal, one at T_1 , the other at T_2 . For, if the number of the free electrons is not very small

indeed compared with the number of the atoms, the transfer of a very slight proportion of these electrons from one part to another of a detached wire would make a notable difference in the state of electric charge and affect greatly the value of F and f .

It is to be noted, also, that the occurrence of a great or small electric concentration, n , at any place in a metal does not imply a proportional state of charge there; for the electrons, in merely getting free from the atoms of the metal, do not change the general condition of charge in their neighborhood. The positive charges remaining on the deserted atoms adjacent are still effective.

(1) *If the gas pressure tendency is toward $n_1R_1T_1 = n_2R_2T_2$:—*

In this case equation (6) holds, and we can form at once a table of values of $(f \div \beta)$ corresponding to chosen values of q .

TABLE I.

CASES IN WHICH EQUATION (6) HOLDS.

q	Rn	$(f \div \beta)$	(Virtual volts per degree C.) 17
0	constant	$-R$	$-86 \times 10^{-6}r$
-1	$\propto T^{-1}$	0	0
-2	" T^{-2}	$+R$	$+86 \times 10^{-6}r$
$+\frac{1}{2}$	" $T^{\frac{1}{2}}$	$-1\frac{1}{2}R$	-129 " "
1	" T	$-2R$	-172 " "
$1\frac{1}{2}$	" $T^{1\frac{1}{2}}$	$-2\frac{1}{2}R$	-215 " "
2	" T^2	$-3R$	-258 " "

17 The values given in the last column are found as follows:

Charge of electron = approx. 159×10^{-22} electro-mag. units.

Force, in dynes, acting on 1 electron in a potential gradient of 1 volt per cm.

$$= 159 \times 10^{-22} \times 10^8 = 159 \times 10^{-14};$$

Value of R for 1 molecule of an ordinary gas = 137×10^{-18} ;

" " " 1 electron = $137 \times 10^{-18} \times r$,

r being some quantity less than 1. Farther on some more definite estimate of the value of r will be attempted.

$$\frac{(\text{Volts per cm.})}{(\text{Degrees " "})} = \frac{f \div (159 \times 10^{-14})}{\beta} = \text{etc.}$$

The variation of electric charge which one might conceivably find along the wire, by means, for example, of a sufficiently sensitive pith-ball electroscope, might be very different from the "virtual potential gradient"; for it is to be remembered that f may be due in part to the specific attraction of the metal for the electrons, this attraction acting as a function of temperature, and it is probable that such action would not be perceptible at any workable distance outside the metal.

(2) If the thermal effusion law, $n_1(R_1T_1)^{\frac{1}{2}} = n_2(R_2T_2)^{\frac{1}{2}}$, holds:—
In this case we use equation (6') and can find values of $(f \div \beta)$ corresponding to chosen values of q' .

TABLE II.
CASES IN WHICH EQUATION (6') HOLDS.

q'	$R\frac{1}{2}n$	$(f \div \beta)$	(Virtual volts per degree C.)
0	constant	$-\frac{1}{2}R$	$-43 \times 10^{-6}r$
$-\frac{1}{2}$	$\propto T^{-\frac{1}{2}}$	0	0
-1	" T^{-1}	$+\frac{1}{2}R$	$+43 \times 10^{-6}r$
-2	" T^{-2}	$+1\frac{1}{2}R$	129 " "
$+\frac{1}{2}$	" $T^{\frac{1}{2}}$	$-R$	-86 " "
1	" T^1	$-1\frac{1}{2}R$	-129 " "
$1\frac{1}{2}$	" $T^{1\frac{1}{2}}$	$-2R$	-172 " "
2	" T^2	$-2\frac{1}{2}R$	-215 " "

It may be that an equation intermediate between (6) and (6') would come nearer to the truth than either (6) or (6'). For it seems probable that thermal effusion of the electrons has some effect in the interatomic spaces, though less effect than it would have in the case of a thin partition pierced by a narrow hole. I shall, however, for the present go on with equation (6), with occasional references to equation 6') and its consequences.

The Thomson Effect:—Taking equation (6) as the condition for electrical equilibrium in a detached wire having a temperature gradient, I shall now find the Thomson effect coefficient, σ , in this metal. This coefficient I shall so define that σdT will mean the mechanical equivalent of the heat absorbed during the passage of the electromagnetic unit quantity of electricity, $\frac{1}{e}$ electrons, if e is the numerical value of the electron charge, from a part of the metal at temperature T to a part at temperature $T + dT$, under the conditions of electrical equilibrium. That is, I am dealing with a reversible process and ignore for the present the consideration of *resistance-heat*, which, according to custom, we may assume to be as small as we please to make it. My only innovation here is the change of sign of σ ,—for example, from + to - in copper and from - to + in iron, because the current of electricity is now thought of as a movement of the negative electrons. In my equations e is to be taken as a positive quantity.

We have to consider the passage of electrons through the region lying between two parallel plane surfaces, each of which is isothermal and also equipotential, the temperatures being T and $T + dT$, respectively. We have to take account of three changes in the energy condition of the electrons during that passage, change of kinetic energy due to the change of temperature, change of potential energy of surrounding electron gas pressure, change of potential energy F due to attractions and repulsions. If R were constant, the first two changes together would equal the mass of the electrons multiplied by the rise of temperature and by the specific heat, C_p , of the electron gas, at constant pressure. We may indeed, if we please, use the terms C_v and C_p ; but, as neither of the specific heats is a constant when R is variable, we should find them of no great service. It is to be noted, however, that, even when R is variable, we have, c being velocity of mean square of the electrons and energy being reckoned in ergs,

$$\text{kinetic energy per gram} = \frac{1}{2} v m n c^2,$$

$$\text{and} \quad p v \quad \text{“} \quad \text{“} \quad \text{“} \quad = \frac{RT}{m} = \frac{1}{3} m n c^2,$$

$$\text{whence} \quad k.e. \quad \text{“} \quad \text{“} \quad \text{“} \quad = \frac{3}{2} \frac{RT}{m}, \quad (11)$$

$$k.e. \text{ per electron} = \frac{3}{2} RT, \quad (12)$$

$$p v \text{ energy per electron} = RT. \quad (13)$$

When, therefore, we have the electromagnetic unit quantity of electricity in the form of $\frac{1}{e}$ electrons entering the region in question at the T surface and issuing at the $T + dT$ surface, we have

$$\text{gain of } k.e. \text{ energy} = \frac{3}{2e} \left[(RT)_{T+dT} - (RT)_T \right] = \frac{3}{2e} \left(R + T \frac{dR}{dT} \right) dT,$$

$$\text{gain of } p v \text{ energy} = \frac{1}{e} \left(R + T \frac{dR}{dT} \right) dT,$$

$$\text{gain of } F \text{ energy (see eq. (8))} = \frac{dF}{e} = \frac{1}{e} (f \div \beta) dT.$$

The total gain of energy by the electrons, which must equal the heat energy absorbed from the metal between the two planes T and $T + dT$, is

$$\sigma dT = \frac{5}{2e} \left(R + T \frac{dR}{dT} \right) dT + \frac{1}{e} (f \div \beta) dT, \quad (14)$$

whence, by use of equations (1) and (6), we get

$$\sigma = \frac{5}{2e}(1+\rho)R - \frac{1}{e}(1+q)R = \frac{k_r}{e}\left(\frac{3}{2}(1+\rho) - \nu\right)T^p. \quad (15)$$

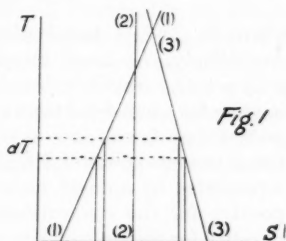
If, on the other hand, we go through the argument regarding σ from the point of view of thermal effusion, as expressed in (6'), where $(f \div \beta) = -R(\frac{1}{2} + q')$, and $q' = \nu + \frac{1}{2}p$, we get

$$\sigma = \frac{1}{e}\left(2(1+\rho) - \nu\right)R = \frac{k_r}{e}\left(2(1+\rho) - \nu\right)T^p. \quad (15')$$

Now on the thermo-electric diagram, as it is usually made, we find three types of lines representing the various metals, all these lines being straight. The character of these representative lines and their inclinations toward each other remain unchanged when we make the diagram in the form shown by Fig. 1, with the temperature axis vertical and the entropy axis horizontal. If we mark the temperature interval dT on line (1)-(1) of this diagram, the area under this portion of the line, between the two verticals extending to the S axis, will represent the amount of heat energy absorbed by the unit quantity of electricity, $\frac{1}{e}$ electrons, in passing along the metal (1) through a rise of temperature dT . This amount of heat is TdS and is a positive quantity for the line (1)-(1). Evidently we have $\sigma dT = TdS$, and, if the (1)-(1) is really a straight line, $dT \propto dS$, and so $\sigma \propto T$. That is, in this case, the ρ of (15) or (15') must equal 1, and this must be true for every metal which can properly be represented on our diagram by a straight line.

For the line (2)-(2) dS is zero and σ also is zero. For the line (3)-(3) the area under dT represents the heat taken from the metal by $\frac{1}{e}$ electrons in going along metal (3) through a fall of temperature dT , and we have $\sigma(-dT) = TdS$, so that σ is negative, though it is still $\propto T$, if (3)-(3) is a straight line.

Dealing, then, with metals represented by such lines¹⁸ as (1)-(1)



¹⁸ If a line is convex upward, as from my own observations I believe the line for iron to be, the indication is that ρ is numerically > 1 .

and (3)-(3), and assuming that we have to do with free electrons, electrons (*B*), only, we should have to conclude that ρ is 1. To determine the algebraic sign of σ we must look to the relative magnitude of ρ and ν . According to equation (15), ρ being 1, we have

$$\sigma > 0, \text{ if } \nu < 3; \sigma = 0, \text{ if } \nu = 3; \sigma < 0, \text{ if } \nu > 3.$$

From (15') we should get

$$\sigma > 0, \text{ if } \nu < 4; \sigma = 0, \text{ if } \nu = 4; \sigma < 0, \text{ if } \nu > 4.$$

Turning back now to equation (2), and assuming that we have to do with (*B*) electrons only, we get as the specific conductivity

$$K_b = k_b F_2(\delta) T^{(\nu - \frac{1}{2}(\rho + 1))},$$

where $F_2(\delta)$ is a factor which increases with rise of temperature. Accordingly, K_b must increase with rise of temperature, unless $\nu < \frac{1}{2}(\rho + 1)$,—that is, unless $\nu < 1$, if $\rho = 1$. But we have just seen that, in order for a metal to have σ negative and proportional to T , ν must be greater than 3, and so $\nu - \frac{1}{2}(\rho + 1) > 2$, which will make K_b proportional to some power of T higher than the second. Metals commonly represented by straight lines on the thermoelectric diagram, with σ positive for the conventional conception of current and therefore negative for the electron conception of current, are copper, silver, zinc and antimony. There may be inaccuracy in taking the lines for these metals as straight, but it is unlikely that this inaccuracy is great enough to account for the absurdity here indicated regarding conductivity. It seems difficult to avoid the conclusion that the conception of free electrons acting alone is insufficient to account for the phenomena of both electric conduction and thermo-electric action.

Accordingly we must presently return to the consideration of those electrons which take part in the action (*A*).

The antagonism between ν and ρ which is to be observed in equation (15) and (15') is rational. Great concentration of free electrons at the hot end of a wire, corresponding to a large value of ν , must tend by gas-pressure of the electrons to give a large value of F at the cold end, so that the term $(f \div \beta)$ in the value of σ (see equation (14)) will be negative. Rapid increase of R , on the other hand, with rise of temperature, corresponding to a large value of ρ , involves large thermal capacity of the electrons and tends to keep σ positive.

The increment of F for any rise of temperature dT along the wire is readily found from equation (8) to be

$$dF = -(1 + q)RdT = -(1 + \rho + \nu)RdT, \quad (16)$$

if equation (6) is followed, and

$$dF = -\left(\frac{1}{2} + q'\right)RdT = -\left(\frac{1}{2}(1 + \rho) + \nu\right)RdT, \quad (16')$$

if equation (6') is followed.

Integrating from T' to T we get from (16)

$$(F - F') = -\left(1 + \frac{\nu}{1 + \rho}\right)(RT - R'T') \quad (16a)$$

and from (16')

$$(F - F') = -\left(\frac{1}{2} + \frac{\nu}{1 + \rho}\right)(RT - R'T') \quad (16a')$$

The difference of potential which might, conceivably, be detected by a sufficiently sensitive electroscope applied to the two ends of the wire in succession would not, probably, be equal to our $(F - F')$; for, according to our assumptions, the value of F is dependent upon the attraction of the atoms for the electrons as well as upon electric charge, and this action of the atoms would perhaps not be effective at any distance from the metal greater than the range of ordinary molecular attraction.

Equilibrium in a Single Unequally Heated Wire

(with regard to both (A) and (B) electrons).

The part played by the (A) electrons in electric conduction has been considered in connection with equation (2). We must now ask what they have to do with thermo-electric action or thermo-electric equilibrium.

It is to be observed that, if we take our single wire as part of a thermo-electric circuit like that indicated in Fig. 2, with a very large resistance, R , introduced at one junction, we shall have a current flowing around the circuit, though conditions as near as we please to those of equilibrium exist in each of the metals M_1 and M_2 . That is, we may assume thermo-electric action, bringing into play the conductive function of the (A) electrons, while keeping all our equations, from (5) to (10) inclusive, just as we have derived and used them with respect to the (B) electrons alone.

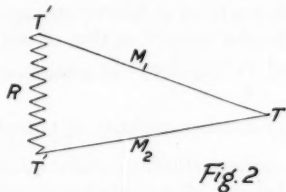


Fig. 2

These equations do not involve the (*A*) electrons, and they must hold irrespective of these electrons, if we have, as we still suppose, conditions very close indeed to those of equilibrium. But as soon as we begin to consider actual flow, however slow it may be, we must take into account the (*A*) electrons and the amount of heat energy they absorb from the metal.

The Thomson Effect:—Let us consider, as before, what happens at and between two equipotential and isothermal surfaces, separated by a distance dl and a temperature interval dT . If we let K_a represent, as before, the part of the specific electric conductivity which depends on the (*A*) electrons, K_b that part which depends on the (*B*) electrons, and $K = K_a + K_b$, we shall have $(K_a \div K)$ as the (*A*) fraction of the current and $(K_b \div K)$ as the (*B*) fraction.

Let the ratio $(K_a \div K)$ be called $(1 - x)$, and $(K_b \div K)$ be called x , just as in a mixture of water and water vapor the proportion of the latter is commonly called x . In the passage of electrons from the bound state to the (*B*) state we have, in fact, a process similar to the evaporation of water, and this analogy is helpful in the present argument.

The total energy of $\frac{x}{e}$ electrons (*B*) at the temperature T is made up of the kinetic energy $\frac{x}{e} \times \frac{3}{2}RT$, the *pv* potential energy $\frac{x}{e}RT$, and the attraction-repulsion potential energy $\frac{x}{e}F$.

The total energy of $\frac{1-x}{e}$ electrons (*A*) at the same temperature is made up of kinetic energy, which I shall assume for the present to be the same¹⁹ as that of an equal number of (*B*) electrons, namely $\frac{1-x}{e} \times \frac{3}{2}RT$; of attraction-repulsion potential energy, $\frac{1-x}{e}F$; and of another quantity of potential energy, $\frac{1-x}{e}\Phi$, due to the attraction of the particular metallic atoms to which the (*A*) electrons individually belong. Φ is a negative quantity; that is, $(-\Phi)$ is the amount of potential energy which an electron gains in being freed from an atom. Let $\Phi = k_\pi T^\pi$, where k_π and π are constants, k_π being negative and π

¹⁹ The (*B*) electrons may be regarded as individuals which have dropped out of the (*A*) class by going astray from the short path leading from one atom to the next atom.

probably so. Accordingly we get, as the total energy of our $\frac{1}{e}$ electrons at temperature T of the metal,

$$E = \frac{1-x}{e} \left(\frac{3}{2} RT + F + \Phi \right) + \frac{x}{e} \left(\frac{5}{2} RT + F \right) \quad (17)$$

$$= \frac{1}{e} \left(\frac{3}{2} + x \right) RT + \frac{F}{e} + \frac{1}{e} (1-x) \Phi.$$

In looking for the amount of heat energy which is absorbed from the metal by our $\frac{1}{e}$ electrons in their passage from T to $T + dT$ through the metal, we must remember that x is a variable, increasing, according to my assumption, with rise of temperature. We have

$$\sigma dT = \frac{dE}{dT} dT.$$

whence

$$\sigma = \frac{1}{e} \left[\frac{3}{2} \frac{d}{dT} (RT) + \frac{d}{dT} (xRT) + \frac{dF}{dT} + \frac{d\Phi}{dT} - \frac{d(x\Phi)}{dT} \right]. \quad (18)$$

It may be well just here to inquire whether the (B) electrons, which we have found to be inadequate when taken alone, are needed at all,—whether the (A) electrons acting alone would serve our purpose. Let us accordingly assume, for the moment at least, that ν and x are each equal to zero. That part of F which is dependent on the free electrons will also be zero in this case, while the other part of F , the part depending on the attraction of the atoms as a function of temperature, will be included in Φ , provided $(-\Phi)$ is now defined as the gain of potential energy of an electron in being taken from an atom in the metal to a point outside the metal. Accordingly we get from (18)

$$\sigma = \frac{1}{e} \left[\frac{3k_r}{2} (1 + \rho) T^\rho + k_\pi \pi T^{(\pi-1)} \right] \quad (19)$$

The first term within the brackets is $+$, according to our assumption regarding R as a function of T . In the second term the factor k_π is $-$, as we have seen before, but the factor π is also $-$, if, as seems probable, Φ diminishes numerically with rise of temperature. We seem, then, with (19) to have no provision for negative values of σ , such as, we know, occur in metals.

Returning, then, to equation (18) and putting

$$x = k_z T^\kappa, \quad (20)$$

with k_z and κ as positive constants, we get

$$\sigma = \frac{1}{e} \left[k_r \left(\frac{1}{2} + \frac{\rho}{2} - \nu \right) T^\rho + k_z k_r (1 + \kappa + \rho) T^{(\kappa + \rho)} + k_\varphi \pi T^{(\pi - 1)} k_z k_\varphi (\kappa + \pi) T^{(\kappa + \pi - 1)} \right]. \quad (21)$$

If we take the point of view of thermal effusion, according to which

$$dF \div dT = -R \left(\frac{1}{2} + \frac{\rho}{2} + \nu \right), \text{ we get from (18)}$$

$$\sigma = \frac{1}{e} \left[k_r (1 + \rho - \nu) T^\rho + k_z k_r (1 + \kappa + \rho) T^{(\kappa + \rho)} + k_\varphi \pi T^{(\pi - 1)} k_z k_\varphi (\kappa + \pi) T^{(\kappa + \pi - 1)} \right]. \quad (21')$$

Neither equation (21) nor equation (21') would permit us to have σ strictly proportional to T ; but we are not sure that σ is strictly proportional to T in any metal. If the terms beyond the first in the second member are small compared with this first term, we may have approximately straight lines on the thermo-electric diagram,—that is, have σ nearly proportional to T , if $\rho = 1$.

Moreover, the presence of $(-\nu)$ in the coefficient of this first term provides for possible negative values of σ , if the first term is really the dominating part of this quantity. Of the other terms, the second and third are positive, according to the assumptions already made, while the fourth may be negative, if π , which is supposed negative, can be numerically greater than κ . I shall assume, for the present at least, that k_z is very small, thus making the second and fourth terms very small. To make k_z small is to make x small, so that I am here assuming that the greater part of the electric conductivity is due to the (*A*) electrons. This assumption accords well with what we know in regard to the temperature coefficient of conductivity. For even with equation (21) we cannot get a negative value of σ proportional to T , a condition approached very closely by several metals, without making $\rho = 1$ and ν greater than 1, so that the K_b term in the value of the conductivity, equation (2), will still increase with rise of temperature. The K_a term in (2) must apparently be the prevailing term, at least so far as the temperature coefficient of conductivity is concerned, in some metals, if not in all.

It is to be observed that the very important part played by ν in the equations (21) and (21') does not imply that n , the number of free electrons per cu. cm. of the metal, is so large as to be of the same order of magnitude as the number of atoms per cu. cm. The value of $(dF \div dT)$, by way of which ν gets into the equations in question, is not dependent upon the absolute value of n at any place, but upon the ratio of the n of one temperature to the n of another temperature. Thus it is possible for a comparatively small number of free electrons to have a great effect upon σ , by way of the (*A*) electrons which are subject to the $(dF \div dT)$ established by the (*B*) electrons.

As to the term $k_{\varphi} \pi T^{(\pi-1)}$ in equation (21) and (21'), although we are hardly at liberty to assume k_{φ} to be small in comparison with $k_{\pi} \pi$, which we suppose to be negative, may be small, and the factor $T^{(\pi-1)}$ is less than T^{-1} . It seems not unlikely, then, that this term is small compared with the T^{ρ} term.

If we are satisfied that equations (21) and (21') accord in a general way with the known phenomena of the Thomson effect, we must next inquire whether either of these formulas will give a good quantitative account of the Thomson coefficient σ as found by experiment in certain metals. Let us consider *lead*, with $\sigma = 0$, very nearly; *cobalt*, with $\sigma = 2000$ ²⁰; and *antimony*, with $\sigma = -1000$. I take cobalt and antimony because they have the limiting values known to me.

Taking the first term in the value of σ as the dominating one, we see that, if we take $\rho = 1$, as we do in other cases, $\sigma = 0$, according to (21), if $\nu = \frac{1}{2} + \frac{1}{2} \rho = 1$ or, according to (21'), if $\nu = 1 + \rho = 2$. Neither 1 nor 2 seems a very improbable value for ν .

Substituting R for $k_{\pi} T^{\rho}$ in this first term we have, approximately, for cobalt,

$$\sigma = \frac{1}{e} \left(\frac{1}{2} + \frac{\rho}{2} - \nu \right) R = 2000 \quad (22)$$

or

$$\sigma = \frac{1}{e} (1 + \rho - \nu) R = 2000 \quad (22')$$

The value of R_{ρ} , reckoned for a single molecule of an ordinary gas, is about 137×10^{-18} . If we for a moment assume this as the value of the electron R in (22) and (22') and take $e = 159 \times 10^{-22}$ in electromagnetic units, and $\rho = 1$, we get from (22), $\nu = 0.77$, and from (22'), $\nu = 1.77$.

²⁰ These are approximately, the values given for the metals in question at 0° C. in the *Recueil de Constantes Physiques* (1913) of the Société Française de Physique.

But it is unlikely that R for the electron is as great as R_g for a gas molecule at ordinary temperatures.

If we take $R = 0.5R_g = 68.5 \times 10^{-18}$, we get

from (22), $\nu = 0.54$, and from (22'), $\nu = 1.54$.

If we take $R = 0.1R_g = 13.7 \times 10^{-18}$, we get

from (22), $\nu = -1.32$, and from (22'), $\nu = -0.32$.

If we put $\nu = 0$, we get

from (22), $R = 32 \times 10^{-18}$, and from (22'), $R = 16 \times 10^{-18}$.

As negative values of ν seem improbable, the indication of this investigation is that in cobalt, at the temperature for which $\sigma = 2000$, R may well be as small as $0.25 R_g$, but is probably greater than $0.1R_g$.

Turning now to antimony we have

$$\sigma = \frac{1}{e} \left(\frac{1}{2} + \frac{\rho}{2} - \nu \right) R = -1000 \quad (23)$$

$$\text{or} \quad \sigma = \frac{1}{e} (1 + \rho - \nu) R = -1000 \quad (23')$$

If we take $R = R_g$, we get

from (23), $\nu = 1.12$, and from (23'), $\nu = 2.12$.

If $R = 0.5R_g$, we have

from (23), $\nu = 1.23$, and from (23'), $\nu = 2.23$.

If $R = 0.1R_g$, we have

from (23), $\nu = 2.16$, and from (23'), $\nu = 3.16$.

Here also, since large values of ν seem rather improbable, the indication appears to be that R is greater than $0.1 R_g$.

On the whole, thus far, it appears that the hypothesis of combined action of (*A*) electrons and (*B*) electrons, with the former playing much the greater part in electric conduction and the latter having a very important function in a metal not uniformly heated, gives a reasonable account of the phenomena of electric conduction,²¹ including change of conductivity with change of temperature, and of the Thomson effect, in pure metals.

It is now time to consider how well the same hypothesis will apply to the phenomena at the junction of two metals, the Seebeck effect and the Peltier effect.

²¹ It seems not unlikely that the change of resistance of metals in melting, in most cases an increase, is due mainly to the change of volume, which also in most cases is an increase. See Appendix for data and discussion.

Conditions of Equilibrium at a Junction of Two Metals at the same Temperature.

Let the two metals be called M_1 and M_2 , and let each be throughout at the temperature T . As the thermo-electric force of an isothermal circuit is zero, whatever the arrangement of the metals, we may assume the transition from M_1 to M_2 to be as gradual as we please to make it, by way of an intermediate stretch of an alloy of the metals, this alloy changing by any law from pure M_1 at one end to pure M_2 at the other end.

If we take the ordinary view of an alloy and think of it as a physical mixture of the component metals in small particles, much larger, however, than the atoms or molecules, we shall have the mean n and the mean R , in the successive cross-sections of the bridge reaching from M_1 to pure M_2 , changing gradually, by the increasing proportion of M_2 particles, from n_1 and R_1 to n_2 and R_2 . It seems reasonable, if not inevitable, to assume that for any given cross-sectional slice of this bridge we shall have

$$\frac{n_1 - n}{n_1 - n_2} = \frac{R_1 - R}{R_1 - R_2}, \text{ or } R = R_1 + (n - n_1) \cdot \frac{R_1 - R_2}{n_1 - n_2}, \quad (24)$$

and

$$\frac{dn}{n_1 - n_2} = \frac{dR}{R_1 - R_2}, \text{ or } dR = dn \cdot \frac{R_1 - R_2}{n_1 - n_2}. \quad (25)$$

For equilibrium of condition of the slice in question, the thickness of which we shall call dl , we must, if we disregard thermal effusion and assume that the free electrons, as a *gas*, tend to uniformity of pressure, have the difference between the electron gas-pressures at the two faces equal to the pull of the virtual potential gradient on all the free electrons in the slice. This consideration, with the reflection that p , the gas pressure of the electrons, is $n R T$, leads to the equation

$$dp = T \frac{d(nR)}{dl} \cdot dl = -n \frac{dF}{dl} dl, \quad (26)$$

whence

$$dF = -TR \frac{dn}{n} - TdR. \quad (27)$$

Substituting for R and dR from (24) and (25), we get

$$dF = -2T \frac{R_1 - R_2}{n_1 - n_2} dn - T \left(R_1 - n_1 \frac{R_1 - R_2}{n_1 - n_2} \right) \frac{dn}{n}, \quad (28)$$

whence

$$F_2 - F_1 = T \frac{R_2 n_1 - R_1 n_2}{n_1 - n_2} \log \frac{n_1}{n_2} + 2T(R_1 - R_2). \quad (29)$$

If R_1 is equal to R_2 , this reduces to the familiar form

$$F_2 - F_1 = RT \log \frac{n_1}{n_2}, \text{ or } \frac{n_2}{n_1} = e^{-\frac{(F_2 - F_1)}{RT}},$$

the Boltzmann equation which we have called (4).

The condition for gas-pressure equilibrium in case of thermal effusion, being $p = (RT)^{\frac{1}{2}} \times \text{a constant}$, becomes now, in the isothermal bridge passing from M_1 to M_2 , $p = R^{\frac{1}{2}} \times \text{a constant}$. If there were no electrical complication, the condition for equilibrium in this bridge would be

$$\frac{d}{dl} \left(\frac{p}{R^{\frac{1}{2}}} \right) = \frac{1}{R^{\frac{1}{2}}} \frac{dp}{dl} - \frac{p}{2R^{\frac{3}{2}}} \frac{dR}{dl} = 0,$$

or

$$dp = \frac{p}{2} \frac{dR}{R}. \quad (\text{See eq. (10)})$$

The actual condition for equilibrium is

$$dp - \frac{p}{2} \frac{dR}{R} = -n \frac{dF}{dl},$$

whence, as $p = nRT$, we get

$$T \frac{d(nR)}{dl} dl = \frac{T}{2} n dR - n \frac{dF}{dl} dl, \quad (26')$$

and so

$$dF = -TR \frac{dn}{n} - \frac{1}{2} T dR. \quad (27')$$

Substituting for R and dR from (24) and (25) we get

$$dF = -\frac{3}{2} T \frac{R_1 - R_2}{n_1 - n_2} dn - T(R_1 - n_1) \frac{R_1 - R_2}{n_1 - n_2} \frac{dn}{n} \quad (28')$$

whence

$$F_2 - F_1 = T \frac{R_2 n_1 - R_1 n_2}{n_1 - n_2} \log \frac{n_1}{n_2} + \frac{3}{2} T(R_1 - R_2). \quad (29')$$

This differs from (29), which was obtained without the hypothesis of thermal effusion, only in having $\frac{3}{2}$, instead of 2, as the coefficient of

the last term. If $R_1 = R_2$, this last term disappears and we have as from (29)

$$F_2 - F_1 = RT \log \frac{n_1}{n_2}.$$

The difference of virtual potential expressed by equation (29) applies to the (A) electrons as well as to the (B) electrons; for it is to be remembered that, even when we have been dealing with a temperature gradient, the rate of change of F has depended not at all upon x , though the Thomson effect was found to be a function of x , as the Peltier effect doubtless will prove to be.

The Peltier Effect:—Referring to equation (17) we see that, when $\frac{1}{e}$ electrons pass reversibly at temperature T from M_1 to M_2 , the gain of total energy of these electrons, which must be equal to the amount of heat energy absorbed by the electrons from the metals at the junction, is

$$Q = E_2 - E_1 = \frac{3 + 2x_2}{2e} R_2 T + \frac{F_2}{e} + \frac{(1 - x_2) \Phi_2}{e} - \frac{3 + 2x_1}{2e} R_1 T - \frac{F_1}{e} - \frac{(1 - x_1) \Phi_1}{e}. \quad (30)$$

Substituting for $(F_2 - F_1)$ from equation (29), we get

$$Q = \frac{T}{e} \left[(x_2 - \frac{1}{2}) R_2 - (x_1 - \frac{1}{2}) R_1 \right] + \frac{T}{e} \cdot \frac{R_2 n_1 - R_1 n_2}{n_1 - n_2} \log \frac{n_1}{n_2} + \frac{1}{e} \left[(1 - x_2) \Phi_2 - (1 - x_1) \Phi_1 \right]. \quad (31)$$

This is the Peltier effect heat at the junction of temperature T .

With thermal effusion equation (30) would hold unchanged, but (31) would become

$$Q = \frac{T}{e} (x_2 R_2 - x_1 R_1) + \frac{T}{e} \cdot \frac{R_2 n_1 - R_1 n_2}{n_1 - n_2} + \frac{1}{e} \left[(1 - x_2) \Phi_2 - (1 - x_1) \Phi_1 \right] \quad (31')$$

The Volta Effect:—It is evident that the equilibrium which we are discussing between two metals at their junction is of the *mobile* type, the superior gas-pressure of the electrons in one metal maintaining a movement of individual electrons from this metal to the other, while the superior "virtual potential" of the second metal has become great enough to maintain an equal movement of other individual electrons

from this metal back to the first, the case being pretty closely analogous to the equilibrium between a liquid and its saturated vapor. A still closer analogy, perhaps, is found in the equilibrium of an isothermal atmosphere over some part of the earth. Individual particles in the upper strata are falling toward the earth under the pull of gravity, but their places are taken by equally numerous molecules projected upward by heat energy from the denser layers below.

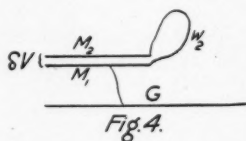
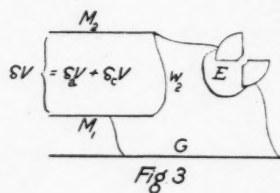
The question now to be considered is, whether our "virtual" potential-difference, $\frac{1}{e} (F_2 - F_1)$ for the electromagnetic unit charge, is the same thing as the Volta potential-difference, which quantity has been the subject of a vast amount of arguing and experimenting for more than a century. In approaching this question let us write

$$\frac{1}{e} (F_2 - F_1) = \delta V = \delta_a V + \delta_c V, \quad (32)$$

where $\delta_a v$ is that part of $\frac{1}{e} (F_2 - F_1)$ which depends on the difference of specific attraction of the two metals for the electrons, and $\delta_c V$ is the part which is due to the difference of electric charge of the two metals.

To give my conception of the Volta potential difference I shall describe an experiment which, if we could work with perfectly clean metals in a vacuum or in a gas absolutely inert, would be easy to carry out, but which, failing this exceedingly difficult condition, must be regarded as imaginary.

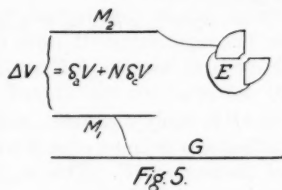
In Figure 3 let M_2 be a plate of metal connected with two quadrants



of an electrometer, E , and with a distant plate, M_1 , of another metal, both M_1 and the quadrants being grounded. For simplicity let us suppose that the quadrants and all connecting wires are of metal (2).

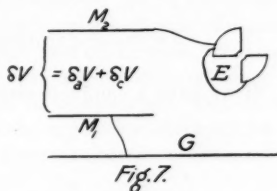
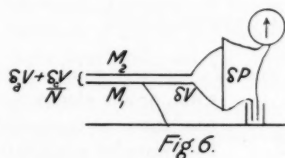
There is, accordingly, no difference of potential between M_2 and the quadrants in Figure 3, but the potential of M_2 exceeds the potential of M_1 by the amount, positive or negative, which we call δV .

In Figure 4, M_2 , disconnected from the electrometer but still connected with the grounded M_1 by the wire w_2 , is brought very near to M_1 , so that the two act as the plates of a condenser. The difference of potential between them is still δV , but M_2 now acquires a considerable charge, Q . The two plates are next disconnected, and M_2 is then removed to its first position, out of range of the condenser action of M_1 , and is connected with the quadrants, as now insulated from the ground, as in Figure 5. The charge Q distributes itself over M_2 and the quadrants, but, as the capacity of this combination is much less than that of M_2 when near M_1 , the potential now exceeds that of M_1 by the amount $\Delta V = \delta_a V + N \delta_c V$, the value of N being greater the less the distance between M_2 and M_1 in Figure 4.



If we assume, as we shall do for convenience here, that the capacity of the quadrants is negligible compared with the capacity of M_2 by itself, we take the capacity of M_2 when near M_1 , as in Figure 4, to be N times the capacity of M_2 by itself.

After grounding M_2 and the quadrants for a moment, thus reducing their excess of potential over M_1 to the original δV , we bring M_2 again to the same position as in Figure 4 and again connect it with M_1 by means of wire of metal (2); but now through a part of this wire flows a



current, so that by a potentiometer arrangement, indicated in Figure 6, we can make the M_1 end of the wire exceed the M_2 end of it by a difference of potential δP . If we make δP such that the difference of potential between M_2 and M_1 in Figure 6 is $\delta_a V + (\delta_c V \div N)$, the charge on M_2 will be precisely what it was after M_2 and E were grounded from the condition shown in Figure 5; that is, when M_2 is separated from M_1 in Figure 6 and is afterward brought to the position and con-

nection of Figure 7, its potential excess above M_1 will be δV , just as it was before the last approach of the two plates.

Now in Figure 6 the M_1 end of the connecting wire, being of metal (2), is at potential δV above M_1 . Accordingly we have whence

$$\begin{aligned}\delta V - \delta P &= \delta_a V + \delta_c V - \delta P = \delta_a V + (\delta_c V \div N), \\ \delta_c V &= \frac{N}{N-1} \cdot \delta P\end{aligned}\quad (33)$$

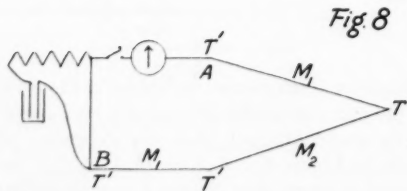
As δP is easily measured, and as N can be made large, we have here indicated a definite, even if not at present entirely practicable, method of measuring δV . This is the Volta potential difference, chemical action excluded.

It is evident that the experiments just described would not give the value of $\delta_a V$ or even show whether such a difference of potential, due to differential attraction of the metals for the electrons, really exists. If it does not exist, if $\delta_a V = 0$, the Volta potential difference is our $\frac{1}{e} (F_2 - F_1)$.

But, according to equation (30), $\frac{1}{e} (F_2 - F_1)$ does not account for the whole of the Peltier effect heat, so that, even if $\delta_a V = 0$, the Volta effect is not so related to the Peltier effect that the value of one can be inferred from the value of the other.

Thermo-electromotive-force of a Complete Circuit.

If we have a complete circuit of M_1 and M_2 , we may think of its total, or net, electromotive force as measured



by means of a potentiometer, and we may with advantage have this potentiometer applied as in Figure 8, having contact with M_1 only, an isothermal stretch of this metal

being joined to M_2 at the T' end. The measurement here suggested

is strictly analogous to measurement of the e. m. f. of a galvanic cell in open circuit.

Our preceding discussion suggests two expressions for this net e.m.f. of the circuit. On the one hand, since we begin and end with the same metal, M_1 , at the same temperature, T' , the difference of F between these two terminals must be independent of the specific attraction of M_1 for the electrons, and must therefore represent the charge-difference of potential, the difference of potential in the ordinary sense, between the terminals. Accordingly we have for the open circuit of Fig. 8,

$$E = \frac{1}{e} \int_A^B dF = \frac{T}{e} \left[\frac{R_2 n_1 - R_1 n_2}{n_1 - n_2} \log \frac{n_1}{n_2} + 2(R_1 - R_2) \right. \\ \left. + \left(1 + \frac{\nu_1}{1 + \rho_1}\right) R_1 - \left(1 + \frac{\nu_2}{1 + \rho_2}\right) R_2 \right] \\ - \frac{T'}{e} \left[\frac{R'_2 n'_1 - R'_1 n'_2}{n'_1 - n'_2} \log \frac{n'_1}{n'_2} + 2(R'_1 - R'_2) \right. \\ \left. - \left(1 + \frac{\nu_1}{1 + \rho_1}\right) R'_1 + \left(1 + \frac{\nu_2}{1 + \rho_2}\right) R'_2 \right] \quad (34)$$

Equation (34'), from (16') and (29'), for the case of thermal effusion, would differ from (34) only in having, as the first term within the brackets containing ν , $\frac{1}{2}$ instead of 1, and in having $\frac{3}{2}$ instead of 2 as the coefficient of the $(R_1 - R_2)$ and $(R'_1 - R'_2)$.

The other way of getting an expression for E is to integrate dQ from A to B in Figure 8, assuming now that a current, due to the thermoelectromotive-force, is flowing in the circuit, with sufficient resistance between A and B , at the low temperature part of the cycle, to absorb there practically all the work done by this current, the resistance of the rest of the circuit being negligible in comparison. But, if we perform this integration, we find that the expression obtained for E reduces to precisely what we already have in (34) or in (34'), as of course it should.

If R were a constant and the same for both metals, and if ν_1 were equal to ν_2 , we should get from each of these equations

$$E = \frac{1}{e} (T - T') R \log \frac{n_1}{n_2}. \quad (35)$$

That is, E would be simply proportional to $(T - T')$; but in order that this relation may hold we must have the representative lines of the two metals, on the temperature-entropy diagram, the same distance

apart at every temperature, which is equivalent to saying that the Thomson effect coefficients, σ_1 and σ_2 , of the two metals must be equal at every temperature.

Examination of equations (15) and (15') shows directly that the conditions just imagined, with respect to R and ν , would make σ the same for both metals. This agreement is important only in so far as it gives evidence that the argument carried through in this paper is self-consistent.

Inspection of equation (34), which expresses the net or total e.m.f. of the circuit, answers in some measure the question raised on p. 72; namely, what conditions of the thermo-electric circuit furnish the mechanism for the production of electric energy at the expense of heat. It is to be noted that this equation makes no reference to the possible tendency of either metal to draw electrons to itself from the other metal, or the possible tendency of hot metal to draw electrons from cold metal, or *vice versa*. The absence of any such reference is rational; for the net amount of work done on any electron in passing completely around the circuit must be independent of any such attraction. It is to be observed also that equation (34) does not contain x , which indicates the relative importance of the (*B*) electrons and the (*A*) electrons in conduction. This omission results from my assumption that the (*A*) electrons have the same value of R , at any given temperature, that the (*B*) electrons have. Further consideration may show this assumption to be unjustifiable, in which case more complicated formulae must replace some of the equations of this paper.

On the other hand, it may appear later that I have made too sharp a distinction between the (*A*) electrons and the (*B*) electrons.

Although the theory set forth in this paper has been formed with no regard to the transverse electromagnetic effects observed in a conductor carrying a current across a magnetic field, it nevertheless, taken in connection with the idea that the free electrons may have something like the Maxwellian distribution of heat velocities, seems to offer some hope of light in these dark places. I must, however, defer discussion of this matter.

APPENDIX.

Sir J. J. Thomson,²² after discussing at length various aspects and consequences of the free electron theory of electric conduction, comes "to the conclusion that the mechanism by which we have supposed the electric current to be conveyed through a conductor is at most only a part and not the whole of the process of metallic 'conduction.' " He continues, "One reason for this conclusion is the large changes which take place in the electrical resistance of some metals on fusion, changes which do not seem to be accompanied by any corresponding change in thermoelectric quality. Thus the conductivities of tin, zinc, and lead at their melting points are, when the metals are in the solid state, about twice what they are in the liquid."

He then goes on to say that the free electron theory, as previously developed by himself and others, would predict for these substances "a Peltier effect between the solid and the liquid metal about half the magnitude of that between bismuth and antimony, and thus, as these effects go, exceedingly large. Now Fitzgerald, Minarelli and Obermeyer, as quoted by G. Wiedemann, '*Elektricität*,' II, p. 289, could detect no sudden change in thermo-electric circuits with these metals when they passed from the solid to the liquid state."

This passage from Thomson, only vaguely remembered, had little if anything to do with the course of my speculations and argument as developed in the paper just concluded; but at the end, being strongly of the opinion that the part played by the free electrons in metallic conduction is a very subordinate one, and that the spaces between the atoms are the great obstacles to electric flow, I naturally turned with curiosity to the question whether the change of resistance in the fusion of metals can be accounted for by the mere change of volume, and so of mean distance between adjacent atoms, which occurs in this change of physical state.

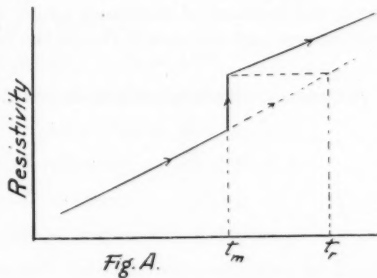
Examination of the available data in this field of inquiry speedily showed one important fact; that, of the twelve metals for which we have trustworthy information concerning change of volume and change of resistance in fusion, ten, cadmium, caesium, copper, lead, mercury, potassium, sodium, thallium, tin, and zinc, increase in both volume and resistivity during fusion, while two, bismuth and gallium, decrease in both properties. Antimony, which decreases in resistance during fusion, may increase slightly in volume during the same change; but this is still in doubt. Northrup, who has been doing excellent

22 *Corpuscular Theory of Matter*, p. 75.

TABLE X.

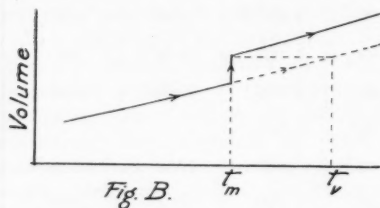
<i>Metal</i>	t_m	$R_l \div R_s$	$V_l \div V_s$	t_r	t_t
Bismuth	270°	0.48	0.967	30°	-565°
Cadmium	320°	1.97	1.047	600°	832°
Caesium	27°	1.69	1.023	112°	107°
Copper	1083°	2.09	1.027	1760°	1240°
Gallium	30°	0.50?	0.98?		
Gold	1063°	2.28	>1?	1950°	1790? ²⁵
Lead	327°	1.92	1.032	675°	716°
Mercury	-39°	4.22	1.036	735°	236°
Potassium	60°	1.61	1.024	174°	160°
Rubidium	38°	1.37	1.023	109°	126°
Sodium	98°	1.51	1.015	210°	171°
Thallium	300°	1.90	1.043	780°	768°
Tin	232°	2.15	1.027	700°	638°
Zinc	420°	2.19	1.04?	800°	1220°

In some cases t_r and t_t were obtained by calculation, in others by a graphical process which is illustrated in Figures *A* and *B*. It is evident that the extrapolations indicated by the dotted extensions of the curves in these Figures are extremely hypothetical, and there was, perhaps, no good *a priori* ground for expecting that t_r and t_t would prove to be even of the same order of magnitude.



²⁵ If $V_l \div V_s = 1.03$.

That they are, in many cases, pretty nearly the same appears to be a fact of some significance, though this significance may be at present obscure. In explanation of and apology for the very marked disagreement of these two hypothetical temperatures in the case of bismuth, and in illustration of the degree of precision needed in the data used, I will say that, if $(V_l \div V_s)$ for bismuth were taken as 0.98,



t_i would be -235° ; and if the ratio were taken as 0.99, t_i would be 17° . Evidently the precise determination of $(V_l \div V_s)$ in a crystalline substance like bismuth is very difficult.

In drawing curves like those of Figures A and B, I sometimes ignored the

course of the curve for the solid just below the melting point, for the reason that for some metals there was a rapid change in the curvature here, as if the melting were already incipient.

Although one can hardly study the table here given without being convinced that the change of volume in fusion is very closely connected with the change of resistance, and is in some large measure the cause of it, examination of the known phenomena of conduction in the solid state shows that we cannot account for changes of resistance by consideration of changes of volume only. For example, the following Table Y, the second, third and fourth columns of which are taken from an article by E. Grüneisen,²⁶ shows by comparison of the fourth and fifth columns that increase of volume is not a very important factor in the increase of resistance which accompanies rise of temperature at constant pressure in the metals here exhibited.

²⁶ Bericht. d. Deutschen Physikalischen Gesellschaft, Heft 6, S. 198 (1913).

TABLE Y.
FOR 0° C.

<i>Pure metals</i>	1	2	3	4	5
	$\frac{1}{v} \left(\frac{dv}{dT} \right)_p$	$-\frac{1}{v} \left(\frac{dv}{dp} \right)_T$ cm. ² /kg	$\frac{1}{w} \left(\frac{dw}{dT} \right)_p$	$-\frac{1}{w} \left(\frac{dw}{dp} \right)_T$ cm. ² /kg	$\frac{1}{w} \left(\frac{dw}{dT} \right)_v$
Al.	70×10^{-6}	133×10^{-8}	40×10^{-4}	43×10^{-7}	37.7×10^{-4}
Ni.	40 “	56 “	60 “	16 “	59 “
Cu.	45 “	75 “	43 “	22 “	42 “
Ag.	54 “	90 “	40 “	39 “	37.7 “
Cd.	90 “	210 “	40 “	100 “	35.7 “
Pt.	27 “	40 “	39 “	20 “	37.6 “
Au.	40 “	59 “	40 “	30 “	38 “
Pb.	88 “	210 “	42 “	150 “	35.7 “

The method by which the numbers of column 5 are found may be shown by an example. We have for aluminium

(1) Coef. of cubical expansion = 70×10^{-6} .

(2) “ “ compressibility = 133×10^{-8} .

∴ No. of atm. (cm²/kg) to keep v const. during 1° heating
= $70 \div 1.33 = 52.5$.

(3) Compression coef. of resistivity = 43×10^{-7} .

∴ Decrease ($-dw/w$) of resistivity caused by 52.5 atm.
= $43 \times 10^{-7} \times 52.5 = 226 \times 10^{-6}$.

(4) Temp. coef. (p const.) of resistivity = 40×10^{-4} .

(5) Temp. coef. (v const.) of resistivity
= $40 \times 10^{-4} - 226 \times 10^{-6} = 37.7 \times 10^{-4}$.

From the data given by Barus²⁷ the following statement for liquid mercury is derived:

²⁷ Bulletin of the U. S. Geol. Survey, No. 92, 74 (1892).

(1)	(2)	(3)	(4)	(5)
180×10^{-6}	300×10^{-8}	8×10^{-4}	300×10^{-7}	-10×10^{-4}

The negative sign of the value of (5) indicates, as Barus points out, that in liquid mercury "the immediate electrical effect of rise of temperature, . . . is a decrement of specific resistance."

Whether a like statement would hold true of other metals in the liquid state we have, so far as I am aware, insufficient data to determine.

SUMMARY.

1. It is pointed out that thermal capacity of the electrons seems to be a necessary condition for thermoelectric action.

2. It is assumed that, through a considerable range of temperature, the number of free electrons per cu. cm. of a metal is represented by the formula $n = k_n T^\nu$, where k_n and ν are constants, T being absolute temperature, and that R , of the equation $p\nu = RT$, "reckoned for a single electron," is represented by the formula $R = k_e T^\rho$, where k_e and ρ are constants, R being less, at ordinary temperatures, for an electron than for a gas molecule.

3. Electric conduction is supposed to be maintained in part by free electrons, (*B*), acting very much like gas molecules in the interatomic spaces of the metal, and in part by other electrons, (*A*), which pass directly from atom to atom, perhaps during collisions, without taking part in the gas-pressure action of the (*B*) electrons.

4. Formulas are obtained for the specific conductivity and the Thomson effect coefficient of a metal, as these properties would be if dependent entirely on the free electrons; and it is found that these two expressions are either incompatible with each other or in discord with observed facts. Argument leads to the conclusion that the free electrons are necessary for the phenomena of thermo-electric action but play an unimportant part in electric conduction.

5. Expressions are found for the Peltier effect and for the difference of "virtual" potential at the junction of two metals, virtual potential being due in part to electric charge and in part to the specific attraction of metals for the electrons. In this connection the Volta effect is discussed.

6. Inspection of the formula obtained for the net e.m.f. of a thermoelectric circuit shows this total to be dependent on the T 's, n 's, ν 's and ρ 's of the system and not upon any specific attraction of metals for the electrons.

7. An Appendix gives data relative to change of volume and change of electric resistance in the melting of metals. It is a general, if not an invariable, rule that change of resistance in melting is of the same sign as change of volume. An attempt is made at a quantitative comparison of these two changes.

8. Attention is called to the fact, first pointed out by Barus, that in liquid mercury rise of temperature without change of volume would bring a *decrease* of resistance.

THE HISTORY OF THE UNITED STATES OF AMERICA

The history of the United States of America is a story of growth and development. It begins with the first settlers who came to the continent in search of a new home. They found a land of vast resources and opportunities, but also one of many challenges. The early years were marked by conflict and struggle, but the spirit of the American people was one of resilience and determination. They fought for their rights and their freedom, and in the end, they won. The United States emerged as a powerful nation, one that would shape the course of world history.

The American Revolution was a turning point in the nation's history. It was a time of great change and upheaval, as the colonies broke away from British rule and established a new government. The war was long and difficult, but the American people were united in their determination to win. They fought for their freedom and their independence, and in the end, they succeeded. The United States was born, and a new era of American history began.

The early years of the United States were marked by a period of rapid growth and expansion. The nation's territory grew from a small strip of land along the Atlantic coast to a vast empire that stretched across the continent. The American people were driven by a sense of adventure and a desire for a better life. They explored new lands, discovered new resources, and built a new nation. The United States was a land of opportunity, and many people came to the continent in search of a new home.

The American people were a people of great faith and belief. They believed in the power of God, and they believed in the power of the American dream. They were a people who sought to improve their lives and the lives of others. They were a people who were willing to sacrifice for their beliefs and their country. The United States was a land of hope and promise, and the American people were determined to make the most of it.

The American people were a people of great courage and bravery. They were a people who were willing to fight for their rights and their freedom. They were a people who were not afraid of困难 and adversity. They were a people who were determined to overcome all obstacles and achieve their goals. The United States was a land of great achievement and accomplishment, and the American people were proud of what they had accomplished.

